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14. ABSTRACT

In this report the development of the use of clusters made of H2 or He as low temperature matrices for the study of chemically unstable species is described. Expriments on the spectroscopy of alkali atoms, alkali dimers and alkali trimers are reported. One section describes the first experiments ever carried out on the Na/He exiplex and another the first detection and spectroscopy of a spin polarized Na trimer. Time resolved experiments on the above mentioned species are also described. As the temperature in these newly developed matrices is substantially lower than in other commonly used matrices, it is anticipated that spectroscopy in cluster will find many applications in the study of chemical metastability. This has important implications for the whole field of high energy materials for rocket propulsion.

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SPECTROSCOPIC INVESTIGATIONS OF ALKALI METAL DOPED HYDROGEN AND HELIUM CLUSTERS

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0 – Supported Personnel and Collaborators

1 – Objectives

2 – Accomplishments/New findings

3 – References

4 – Publications

5 – Interactions

6 – Honors and awards

0 – <u>Supported personnel and collaborators</u>
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    J. Reho (P.U. grad student), Dr. F. Stienkemeier (PDF)
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1_ <u>Objectives</u>

In view of the possible application to improving the propellant properties of solid hydrogen by seeding with light metal atoms, the mobility and other physical properties of atomic and molecular species dispersed in condensed hydrogen has been in recent years one of the main themes of research within the High Energy Density Materials (HEDM) program. A substantial effort has been directed towards the determination of the maximum atom concentrations that can be achieved, the dopant atom-hydrogen interactions and the mobility of the dopants in solid hydrogen.

The experiments described in this report utilize hydrogen clusters instead of the bulk condensed phases as a matrix for the study of these physical interactions for several reasons. First, hydrogen clusters can be doped with metal atoms in a more controlled way than the bulk condensed phases. Second, there is the possibility that a solid matrix, prepared by deposition of metal-doped clusters will show better storage properties (lower diffusion of the dopant) than the solid phase prepared by co-condensation. Finally, since the clusters are finite-size systems, they lend themselves to theoretical simulation more easily than polycrystalline solids where a larger, uncharacterized variety of defects may be present. In parallel with the hydrogen studies metal-atom-doped liquid helium clusters are also being studied because they offer the possibility of synthesizing unstable species such as clusters of spin-aligned atoms, metal atom-hydrogen oligomers and metal atom-helium oligomers. The study of the latter has led us to obtain experimental confirmation of the fact that spin-orbit coupling plays a role in the recombination of some atoms to form their dimers producing small entrance-channel barriers due to the mixing of binding with repulsive states (see below). Since it is becoming clear that, because of the highly quantum nature of solid hydrogen, the rate of diffusion of atomic species is relatively high, we have redirected our efforts toward the study of light dopants, the (re)combination of which may be hindered by spin-orbit effects allowing, therefore, for the achievement of a stable solid propellant with high dopant concentrations.

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2_ Accomplishments/New Findings

2.1_ Description of the instrumentation

Hydrogen and helium clusters are produced in a supersonic expansion and are subsequently doped with alkali metal atoms by passing the cluster beam through a scattering cell that contains a small vapor pressure ($\sim 10^{-2}$ Pa) of the metal of interest. During the past year, there have been two main changes to the experimental setup. First, the output of the laser induced fluorescence (LIF) detector has been modified so that either the usual photomultiplier (PMT) or a monochromator equipped with a charge coupled device (CCD) detector could be used to carry out spectroscopic measurements on the doped clusters. Second, an ortho-para catalytic converter has been installed to study the influence of the J=0/J=1** composition of hydrogen clusters both on fluorescence and beam depletion spectra.

A schematic of the experimental apparatus is given in figure 1. Helium clusters are produced in a molecular beam by expanding the gas through a 10μm nozzle at a temperature of 14-30 Kelvin. Stagnation pressures of 3.5-10 MPa are utilized to produce helium clusters with a median size of 10^3 to 10^4 atoms per cluster. Hydrogen clusters are produced at nozzle temperatures of 40-120 Kelvin and stagnation pressures of 2.9MPa. These expansion conditions lead to the formation of clusters with a size distribution similar to that of helium. Prior to expansion the hydrogen gas is passed through an ortho-para converter consisting of an alumina-supported transition metal catalyst. Assuming the flux to be slow in comparison to the conversion rate (our case), the ortho-para ratio is determined by the equilibrium thermal distribution at the converter temperature, which can be set to any value from 300 K down to 20 K (The corresponding J=1 fraction changes from 75% to 0.2% for H_2 and from 33% to 2% for D_2). The source chamber containing the cluster beam source is backed by a 32,000 l/s diffusion pump while the detection chamber is backed by a 5,000 l/s diffusion pump. The clusters are doped by passing through two collinear pick-up cells directly downstream of a 400μm collimating skimmer. Each pick-up cell is attached to a separate heated tube that transfers the alkali vapor from an oven to the cell. The ovens are heated to establish an alkali pressure of 10^{-3}-10^{-1} Pa in the pick-up cells. The cells are kept at a temperature that is 100 degrees higher than the ovens to avoid distillation and dimer formation. The clusters become doped through the pick-up of one or more alkali atoms without being appreciably deflected from their path. The use of two pick-up cells allows molecular alkali species containing two different alkali atoms to be formed. The cluster beam is then intersected at 90 degrees with the baffled output of a continuous wave dye or a Ti:Al_2O_3 laser. The fluorescence is then collected with a two mirror LIF detector of standard design and is detected with a cooled photomultiplier, irrespective of its wavelength. The output pulses produced by the multiplier are directed to a discriminator and amplifier and stored in an electronic counter. As an alternative, the collected fluorescence can be sent to a monochromator equipped with a liquid nitrogen cooled CCD detector to resolve the emission spectra of the investigated species.

** the ortho-para nomenclature refers to the nuclear spin statistics of the hydrogen molecule. Since symmetry constrains directly relate the nuclear spin to the parity of the rotational quantum number J, and since at low temperature only the states with J=0 (for p-H_2 and o-D_2) and J=1 (for o-H_2 and p-D_2) are populated, we will use the two notations as equivalent.

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The very low noise, wide detection area, and high spatial resolution characteristics of the CCD detector made it possible to collect high resolution spectra at intensities as low as a few photons per second per frequency unit in a reasonable time (5 to 30 minutes). This contributed greatly to a more complete picture of the system under investigation.

A surface ionization detector, located beyond the LIF detector, is used to acquire spectra of the doped clusters by measuring the beam depletion induced when the laser is on resonance with an alkali transition. The absorption of a photon by an alkali atom residing on the clusters causes the atom to desorb from the cluster surface. This will result in a net beam depletion detected by the surface ionization detector. Alternatively, if the atom resides in the cluster any amount of quenching or red shift of the emission (versus the excitation) spectrum will cause the evaporation of large numbers of He atoms or hydrogen molecules which in turn will also produce beam depletion. Finally the surface ionization detector is also used to establish the optimum source conditions for alkali pick-up by the clusters.

We have also set up a ring doubling system for producing narrow band ultraviolet radiation from the output of the continuous wave titanium sapphire ($Ti:Al_2O_3$) laser. This system uses a ring cavity to provide an intracavity power enhancement of the fundamental radiation produced by the $Ti:Al_2O_3$ laser. We have purchased two high efficiency LBO crystals for the ring doubler which allow us to double the fundamental light in the range of 725nm - 825nm to produce tunable UV light in the range of 362nm - 413nm. The ring cavity of the doubler produces an enhancement of the fundamental light of approximately a factor of 70 which gives a doubling efficiency of greater than 10% at the center wavelength of the LBO crystal. Using 0.5-1 W of fundamental power, approximately 50-120mW of scannable UV radiation with a linewidth of less than 5 MHz can be obtained. This doubling system coupled to the $Ti:Al_2O_3$ laser allows us to perform high resolution spectroscopy of a wide range of organic molecules and metallic clusters embedded in the helium cluster matrix.

The laser system and necessary electronics used in the time-resolved studies of the Na*He excimer is shown schematically in Figure 2. A mode-locked, frequency-doubled YAG laser (Quantronix 416) synchronously pumps a folded-cavity dye laser (Spectra-Physics 3500), producing pulses of 10-12 ps full width at half maximum as determined by autocorrelation. The dye laser's natural repetition rate of 75.7 MHz is reduced to 12.3 MHz by means of a home-built "pulse-picker". Laser-induced fluorescence is detected by a single mirror optic (as opposed to our cw experiments in which a double mirror optic is used) and transported to a Microchannel Plate Detector (MPD) (Hammamatsu R2807U-07) through a multimode, incoherent fiber bundle. Wavelength selection is achieved through the use of band pass filters inserted in front of the microchannel plates. Lifetime measurements use the reversed time-correlated single photon counting technique and have a time resolution of 200 ps.

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The fluorescence signal from the MPD is amplified by 2GHz bandwidth preamplifiers and passes through a constant fraction discriminator (Tennelec TC 454) which provides the start signal of a Time-to-Amplitude Converter (TAC) (Ortec 457). The laser pulse that triggers the fluorescent event is detected by a fast photodiode, amplified and appropriately delayed, and processed by a constant fraction discriminator. This signal is then used as the stop signal in the TAC. This 'reverse' method insures that each 'start' pulse is followed by a 'stop' pulse inside the time window of the TAC. In this reversed configuration, high laser repetition rates can be used without causing pile-up error. The output of the TAC is processed by a multichannel analyzer (Nucleus II) and binned, thus compiling our experimental histograms which give the emission intensity as a function of time after each excitation pulse.

The second series of time-resolved experiments, in which the dynamics of the sodium quartet trimer doped onto He clusters are being studied, uses an improved laser scheme. Here the mode-locked frequency-doubled YAG (now a Coherent Antares) synchronously pumps either of two cavity-dumped folded cavity dye lasers (Coherent 700 lasers, Coherent 7201 cavity dumpers) which eliminates the need for an external pulse-picker and allows a thirty-fold build-up of the instantaneous power of each pulse inside the cavity in comparison to the non-cavity-dumped configuration The usable laser power is thus improved by more than two orders of magnitude while the dye lasers are run at the lower repetition rate of 4 MHz. With the higher powers, pump-probe experiments can be carried out.

2.2_ Alkali atoms on helium clusters

The interaction between an alkali atom and a helium atom is the weakest known van der Waals interaction (~ 1 cm^{-1}). For this reason, for alkali atoms both in liquid He and in finite size He clusters, surface states are predicted to be more stable than solvated states.

In the past 3 years, Laser Induced Fluorescence (LIF), Dispersed Fluorescence (DF), and Beam Depletion (BD) spectra of Li, Na, and K atoms (which we will collectively call chromophores) attached to large He and hydrogen clusters have been measured (as an example the three types of spectra for Na on (He)$_N$ are shown in fig.3).These three techniques offer complementary information that allows the complete spectroscopic characterization of these systems.

It is important to mention that LIF and BD spectra of Li and Na are identical after appropriate spectral scaling. For K, there are technical difficulties in collecting all the fluorescence and a fair comparison of the two spectra has not yet been made.

Also taking into account the DF measurements we can conclude that in He clusters:

1. Non-radiative decay of the excited chromophore back to its ground state is negligible. This is not the case for similar systems (e.g. alkali atoms on hydrogen clusters).

2. Virtually all the chromophores are desorbed from the cluster as a consequence of the excitation or the de-excitation process.

3. Both LIF and BD spectra are true absorption spectra for the alkali/cluster system.

A theoretical model [STI96] making use of the "frozen cluster approximation", developed in collaboration with S.I. Kanorsky (Max Planck Institute, Munich) accounts for the position (and to a limited extent for the intensity) of the observed features in the absorption spectra; it can also correctly separate the contributions of bound-bound and bound-free transitions, and demonstrates that the reported measurements provide important benchmarks for testing interaction potentials and calculation schemes.

2.3_ Alkali atoms on hydrogen clusters

a) Beam Depletion Spectra. BD spectra of alkali atoms on hydrogen clusters are shown in fig 4. By comparison with the He cluster case (section 2.2), we believe that these spectra are total absorption spectra, and therefore we present them first.

BD spectra of Li, Na, and K on hydrogen clusters, all share several common features that make them very similar. Like their counterparts in He clusters, they have a slightly red shifted maximum, relative to the position of the gas phase lines, and are asymmetrically broadened with a long tail to the blue. Since the alkali-hydrogen interaction strength is one order of magnitude larger

than the alkali-helium one, so are the shifts and widths of the spectra. In particular, while the fine structure splitting was readily resolved for Na and K on He clusters, in the case of hydrogen it is totally washed out by the stronger chromophore-cluster interaction. It can also be observed that while absorption spectra of alkali atoms on He clusters present a very sharp threshold slightly to the red of the atomic D_1 line, in the case of hydrogen the spectra have a long low energy tail, suggesting that lifetime broadening might be present (see below).

As in the helium case, we infer a surface location for the chromophore based upon the small red shift and moderate broadening. Recent theoretical predictions [ANC95] are inconclusive about whether energy is lower for alkali atoms on the surface or solvated in the cluster.

Experimental [FAJ93] and calculated [CHE96 CHE97 SCH93A SCH93B] absorption spectra are available for comparison only for the case of lithium. Experimental absorption spectra of Li in solid hydrogen matrices have similar shape and red shifted position of the maximium as our spectra, but are more than twice as broad. Theoretical (static) calculations poorly predict the position of the absorption maximum, particularly for solvated states, but do much better for the width of the absorption profile. Not surprisingly, solvated states are predicted to have broader absorption spectra than surface states; the width of our spectra are intermediate between the two cases. We tentatively conclude that alkali atoms (or at least lithium) are located on the surface of the cluster, and that a broadening mechanism not taken into account by the static theoretical simulations (see above) is responsible for the discrepancies. A paper summarizing these results has been published in the J. of Phys. Chem. [CAL98].

b) Laser Induced Fluorescence Spectra. Contrary to the He case, LIF spectra of Li, Na, and K attached to H_2 clusters show no resemblance with BD spectra (fig. 4) and are less intense than their He counterparts by at least 2 orders of magnitude. Both these facts imply that most of the excited chromophores return to their ground state via non radiative transitions (quenching) or else that most emission is red shifted outside our detection window. Further evidence comes from dispersed fluorescence measurements which detected only free atom fluorescence (desorbed from the cluster after excitation). This implies that, unless the atoms are immedietely expelled from the cluster, quenching becomes the dominating mechanism for decay.

LIF spectra of different chromophores are qualitatively similar. They all contain sharp features near the gas phase lines, and one or more broad bumps shifted to the blue by several hundred cm^{-1}. The origin of the sharp features is not clear at present, but they may reflect modulations in the nonradiative decay rate with energy. Time resolved experiments currently in progress (see below) may shed some light on this problem.

A comparison of the broad blue shifted bumps with the corresponding features in the He cluster spectra, taking of course into account that the larger alkali-hydrogen interactions, suggests

that the chromophores are also located on the surface of the hydrogen clusters, and that only those which are immediately desorbed from the cluster contribute to the LIF spectra (see above).

c) *ortho-para* substitution and isotopic effects. To date, computer simulations of the spectra have only been performed for clusters of *para*-hydrogen (100% J=0), but most experiments have been performed with normal-hydrogen (75% J=1). Therefore, we have studied the effect of the J=1 concentration on the experimental spectra, in an attempt to improve the contact between theory and experiments.

The difference observed in the BD spectra at different *o-*, *p*-H_2 concentrations are not dramatic. Much larger changes are observed for LIF spectra, where the intensities of some spectral features are closely linked to the fraction of *p*-H_2 present in the cluster (fig. 4). This is not surprising, as a small change in the cluster-chromophore interaction potentials can strongly affect the (small) fraction of atoms which survive the quenching process. To our knowledge, no calculations or previous experiments have examined the different quenching efficiencies of *o-* and *p*-H_2.

Similar trends, i.e. small differences for the BD spectra and drastic changes in LIF spectra have been observed when replacing H_2 with D_2. Since quantum effects are less important for D_2, D_2 clusters are better candidates for classical molecular dynamics simulations.

2.4_ Alkali/Hydrogen complexes in He clusters

As we have explained in the preceding sections, hydrogen clusters have shown a remarkable ability to quench the fluorescence of the excited alkali atoms.

To understand the quenching process it would be useful to obtain the spectrum of alkali-atom/hydrogen complexes containing only one or a few H_2 molecules. These complexes are however next to impossible to prepare with conventional techniques. As explained above He clusters are particularly suitable to prepare unstable and weakly bound species. Therefore we used the multiple pick-up technique to prepare Na-$(H_2)_n$ complexes on the surface of He clusters.

Fig. 5 shows the total Na fluorescence yield as a function of the background pressure of H_2. At a pressure where the fluorescence is attenuated by a factor of 1/e, less than 10 H_2 molecules per cluster are estimated to be picked up in average by the He clusters.
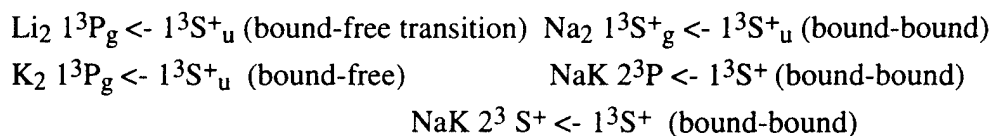
BD spectra obtained at high H_2 background pressure are very similar to those measured for Na atoms on pure H_2 clusters, but the maximum is unshifted, rather than red shifted, with respect to the gas phase lines. We note that the calculated absorption spectra of Li on small H_2 clusters are also less red shifted than experimental spectra of Li on large H_2 clusters, and we suggest that these spectra of M-$(H_2)_n$ on He clusters can be more readily compared to feasible theoretical simulations.

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2.5_ Alkali dimers on helium clusters

When a helium cluster picks up two alkali atoms, a dimer can form on the surface. Alkali dimers can exist in two states: singlet and triplet, depending on the spin alignment of the valence electrons in the molecule. In absence of spin relaxation (i.e. in a pure helium cluster) the probability to form a triplet is 3 times as large as that of forming a singlet. Furthermore, the covalent bond of a singlet Na_2 molecule is over thirty times stronger than the van der Waals bond of the triplet. The binding energy released upon bond formation must be dissipated into the cluster. Deposition of this energy into the helium clusters causes evaporation of the or helium atoms and perhaps the alkali molecule to requilibrate the cluster temperature at 0.4 K [HAR95]. If the cluster is small or if a sufficiently large quantity of energy is dissipated, the cluster will be completely destroyed. Because of the difference in binding energy, the survival of the weakly bound species will be significantly favored over the strongly bound molecules. It is this general property of helium clusters, of allowing the formation of very weakly bound complexes and novel spin species, that we want to exploit for the study of novel high spin molecules and the detection of small barriers that may exist in the formation of aggregates of light atoms and their bimers.

During the last three years, we have explored a variety of different electronic transitions in several different triplet alkali dimers. The low-lying electronic states in the triplet manifold of the homonuclear dimers Li_2, Na_2, K_2 and the heteronuclear dimer NaK have been studied with vibrational resolution. Both bound and unbound excited electronic states have been observed. Heteronuclear dimers are formed by the use of two collinear pick-up cells each containing a different alkali vapor. Because of the small polarizability of helium, the vibrational frequencies in both the lower and upper electronic states remain almost unchanged in the presence of the cluster. Therefore spectral shifts are very small ($\sim$2 cm^{-1}).

The following electronic transitions have been observed for triplet alkali dimers on helium clusters:

Li_2 1^3P_g <- $1^3S^+_u$ (bound-free transition) Na_2 $1^3S^+_g$ <- $1^3S^+_u$ (bound-bound)

K_2 1^3P_g <- $1^3S^+_u$ (bound-free)   NaK 2^3P <- 1^3S^+ (bound-bound)

NaK $2^3 S^+$ <- 1^3S^+ (bound-bound)

As an example, the Na_2 $1^3S^+_g$ <- $1^3S^+_u$ transition is shown in Figure 6. The accurate spectroscopic data obtained in these experiments are being used in determining the detailed interaction potentials in the triplet manifold of the homonuclear and heteronuclear alkali dimers [HIG98] In particular, the data from the bound-free transitions of Li_2 and K_2 can (with a knowledge of the *ab-initio* transition dipole function) be directly inverted to give the excited state potential energy surface, providing an accurate test of theoretical potentials [MAG93].

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Emission spectra have been obtained for the above transitions and reveal two surprising features that appear to be characteristic of alkali molecules on helium cluster surfaces. First, the emission spectrum of the Na_2 $1^3S^+_g$ -> $1^3S^+_u$ transition reveals a vibrational cooling process in the excited state of the dimer. If, for example, the v'=11 vibrational level of the excited electronic state is excited, emission is observed from all the 10 levels below the excitation frequency. The second common feature among the emission spectra is the presence of fluorescence that appears at higher energies than the excitation photon energy. This emission can be assigned to various singlet electronic transitions of the dimer. This phenomenon results from a curve crossing between the triplet and singlet electronic manifolds facilitated by the presence of the helium cluster surface and will be explored in more detail in the following section.

Despite the selectivity in the survival of the weakly bound triplet states, we have been able to observe electronic transitions in both singlet Na_2 and K_2 formed on helium clusters. The general structure of the vibrational bands of the singlet transitions appear to be inherently different from those of the triplet electronic transitions. The spectrum of the $1^1S^+_u$ <- $1^1S^+_g$ transition of Na_2 is shown in figure 7 with a detailed view of an individual vibrational band. Similar to what happens for a chromophore impurity in a solid, each band consists of a narrow zero-phonon line followed by a broad phonon side-band extending to higher energies. In addition to this structure, several peaks appear to slightly higher energies than the zero phonon line which can be correlated with the excitations that occur in bulk superfluid helium (rotons and maxons [HAR96]. Decreasing the mean cluster size in the beam by increasing the nozzle temperature, reveals that some sodium dimers do not completely cool after their formation and instead remain in excited vibrational states on the cluster. The use of small helium clusters as a useful tool for producing substantial directed fluxes of vibrationally excited species is presently being explored in our laboratory.

Emission spectra of the $1^1S^+_u$ -> $1^1S^+_g$ transition also reveals the presence of vibrational cooling of the excited dimer on the helium clusters. The modeling of the emission spectrum using the calculated energy levels of this well-known molecule allows the derivation of the time average populations of each individual vibrational level. We have used this data to fit a rate model for the relaxation, but a unique solution will require the addition of time resolved measurements to distinguish direct from sequential population of the lower states.

2.6_ High resolution spectroscopy of species formed on and desorbed from helium clusters

One of the surprising results obtained in the course of this work was the observation that a fraction of the molecules formed on the clusters' surface desorb at very low velocity, reaching in this way the laser crossing region and allowing the acquisition of high resolution, rotationally resolved spectra that are free from the influence of the helium cluster [STI95]. This increases

tremendously the usefulness of helium clusters as a preparative tool for the weakly bound and high spin complexes described in this proposal. Using this method, we have, for sake of comparison, obtained the high resolution, rotationally resolved spectrum of the $1^3S^+_g \leftarrow 1^3S^+_u$ transition of Na_2 which, due to the difficulty of producing these weakly bound species is one of very few detected directly in the gas phase [FAR96]. Along with the observation of the rotational structure the spin-spin, spin-rotation, and hyperfine splittings can be observed in our spectrum. (see fig. 8).

While the line positions of the $1^3S^+_g \leftarrow 1^3S^+_u$ transition of Na_2 occur at their precise gas phase locations, an additional rotationally resolved spectrum is observed approximately 23 cm^{-1} blue-shifted with respect to the band origin of the Na_2 transition. This spectrum is observed on each vibrational band of the dimer and possesses a high resolution structure that is significantly more complex than the bare dimer transition. It is probable that this spectrum is due to a previously unobserved complex of the triplet Na_2 molecule desorbed from the helium cluster carrying an additional He atom. A calculation using a model potential energy surface of the $1^3S^+_u$ Na_2He triatomic complex made of two-body potential energy terms reveals that this system is bound, but only by 1.1 cm^{-1}. A more accurate modeling of this molecule that includes the effect of three-body forces in the calculation of the dynamics is in progress.

2.7_ Quartet state alkali trimers on helium clusters

While the doublet state of Na_3 has been the focus of previous molecular beam studies [ERN95], the quartet states of this molecule (made of three sodium atoms with parallel spins) had previously never been observed. In a beam of helium clusters, the quartet state will be highly favored in its survival on the cluster surface due to its significantly lower binding energy (800 cm^{-1} vs 9000 cm^{-1} for the doublet). In fact, the $2^4E' \leftarrow 1^4A_2'$ electronic transition of quartet Na_3 (shown in figure 9) is the strongest molecular transition that we have observed on alkali-doped helium clusters. The emission spectrum of this transition reveals three different channels of fluorescence, two of which are at higher energy than the excitation energy.

Direct fluorescence occurs to the lowest quartet of Na_3 (see below) which competes with a non-adiabatic curve crossing into the doublet manifold of the sodium trimer. The latter process is one in which an electron flips its spin in the excited electronic state, resulting in covalent bond formation and liberation of energy that causes the trimer to dissociate into an atom and a singlet sodium dimer. The electronic energy can localize on either the atom or dimer product, leading to the two different fluorescence channels. This provides an ideal system for the study of unimolecular reaction dynamics since this simple 3-electron reaction can be initiated with a laser pulse. The corresponding transition has also been observed in K_3 which allows a direct measurement of the influence of the spin-orbit coupling in the molecule to the rate of spin conversion [HIG96A]. Whereas 20% of excited Na_3 trimers fluoresce to the lowest quartet state,

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only 8% of K_3 molecules remain unreacted due to the larger matrix element of the spin-orbit coupling between the doublet and quartet states.

Analysis of the direct fluorescence to the lowest quartet state of Na_3 has provided insight into the effect of three-body forces in van der Waals systems. The knowledge of the vibrational energy level structure of the $1\,^4A_2{'}$ state derived from the spectroscopic data has provided a sensitive testing ground for the accurate determination of the three-body component to the potential energy surface. The potential energy surface was calculated at the coupled cluster level of theory with single, double, and non-iterative triple excitations (CCSD(T)). The results reveal that the quartet trimer is bound in a D_{3h} configuration by 850 cm^{-1} relative to three free sodium atoms. The bond length is found to 4.4 Å which is significantly contracted from the triplet dimer bond length of 5.09 Å. At the equilibrium configuration, it is found that more than 80% of the binding energy results from non-additive effects. This situation has to be contrasted with the noble gases where at the equilibrium configuration (probably because of the steepness of their repulsive walls) 3-body effects are a factor of 10 smaller [HIG96B].

2.8_ Time-resolved spectroscopy of the formation of the Na*He excimer

The excitation and dispersed emission spectra of Na atom on He clusters have been previously measured in our laboratory. The excitation spectrum obtained by integrating over the complete emission spectrum is illustrated in Figure 10. It is seen that the spectrum begins slightly to the red of the free Na $3P_{1/2,\ 3/2} \leftarrow 3S_{1/2}$ lines and exhibits a long tail on the blue side. The dispersed emission spectra consist of two main features, the relative intensities of which change as a function of the excitation frequency. The first feature has an instrumentally limited linewidth and corresponds to the emission of gas-phase Na* atoms desorbed from the cluster surface upon excitation, labeled as 'bound-free' in the Figure 10. The second feature is broad and structured with intensity spanning the range from 14200 cm^{-1} to 16800 cm^{-1} and is labeled as 'bound-bound' as it has been ascribed to a non-desorbing species. Measurements of fluorescence rise and fall times using reversed time-correlated single photon counting were first made at several points in the excitation spectrum collecting atomic ($16980 \pm 145\ cm^{-1}$) fluorescence. The results are presented in Table I. The data shown in the top half of Table I correspond to excitation to the blue of the atomic lines while collecting the Na gas-phase fluorescence. The resulting decay times were centered around 16.3 ns, in excellent agreement with the known radiative lifetime of the Na D lines , confirming the ability of the instrument to provide accurate lifetimes. Times of 50 ps and 70 ps were found for the florescence rise times (i.e., mean time of the onset of fluorescence) under the same conditions.

Fits to emission from excitation of gas phase Na atoms (in which the rise should be instantaneous) yielded rise times of under 20 ps. Thus we note that the expulsion times of the excited Na atoms from the cluster appear to be larger than our instrumental resolution. These times will be more confidently quantified using pump-probe experiments, which are planned for the near future.

Previous dispersed fluorescence experimentation had uncovered a broad red emission arising from excitation of the Na atom on the cluster surface. Collection of this red-shifted ($15800 \pm 125\ cm^{-1}$) fluorescence yields curves that give rise times strongly dependent on the excitation wavelength, but fall times ranging from 19 to 21 ns, which is longer than the free atom value. Using a constant dipole approximation, taking into account the emission wavelength, a predicted lifetime of 20 ns is obtained, in excellent agreement with the observed value. This implies that there is negligible quenching of this emitting species by the He cluster, in dramatic contrast to the complete quenching observed for Na* in bulk liquid ^{4}He.   As a result, we were able to conclude that this red emission was due primarily to a species emitting in the gas phase; quenching (and thus a decrease in lifetime) would otherwise have been observed.

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Figure 11 shows the dispersed emission spectrum observed following excitation of Na at 16975 cm^{-1}, referred to above as the "red emission". The vertical emission from the lowest four bound states produced by the well of the (A)$^2\Pi$ state of NaHe emitting onto the repulsive wall of its ground (X)$^2\Sigma$ state using the NaHe potentials of Pascale give excellent agreement with the observed emission spectrum. This calculation was performed using the BCONT program of R. J. LeRoy. This result, combined with the lack of quenching reported above, justifies the assignment of this red emission as arising from the bound-free transition of an isolated Na*-He complex. We have performed similar fits to observed emission spectra following excitation from several different wavelengths. In all cases we obtain an excellent simulation of the observed spectrum. Table II shows the relative $^2\Pi$ vibrational populations that result. We see that excitation with higher excess energy results in increased population in the higher vibrational levels of the Na*-He exciplex.

We now turn our attention to the rise times observed when the red emission centered at 15800 cm-1 is monitored. (See lower half of Table I). For excitation energies to the blue of the atomic J = 3/2 line, the observed fluorescence is successfully fit to a model with a single rise time, which is found to be 70 ps, only slightly longer than the rise time observed for the atomic emission. This argues that following such excitations, the formation and desorption of the excimer occurs rapidly, suggesting that the desorption is directly coupled to the formation process. As we move the excitation wavelength to the red of the J = 3/2 atomic line, we find that to successfully fit the observed fluorescence signals, we must use two rise times. One component of the emission (the amplitude of which decreases as the excitation is moved to the red) also has a 70 ps rise time. However, the second component rises much more slowly (~ 700 ps).

An expanded view of the long range A$^2\Pi$ and B$^2\Sigma$ Na-He potentials as calculated by Pascale are shown in Figure 12. This calculation, shown as a thin line in the figure 12, neglects spin-orbit interactions, and thus produces a single $^2\Pi$ surface. Following Takami[17] we account for spin-orbit effects by introducing a constant perturbation equal to the asymptotic Na ^2P spin-orbit splitting of 17.19 cm^{-1}. The spin-orbit operator mixes the $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}$ states, leading to the three curves given in Figure 12 as thick lines which are labeled by their dominant character at short R. We thus see that there are two curves correlating with the formation of the Na*-He exciplex. While the $^2\Pi_{3/2}$ surface is purely attractive at long range, the $^2\Pi_{1/2}$ surface has a small 'outer' well of ~ 0.5 cm^{-1} at R = 9Å as well as a barrier of height 0.19 cm^{-1} relative to the $^2\Pi_{1/2}$ asymptote. This barrier can be understood to arise from the spin-orbit mixing of the $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}$ surfaces, as well as from the fact that the Pauli repulsion on the $^2\Pi_{1/2}$ curve becomes significant at larger distances than the attraction on the $^2\Pi_{1/2}$ surface. We note here that the cluster-Na* potential (calculated in the frozen cluster approximation) predicts that the cluster-Na* $^2\Pi$ excited state has a minimum with the Na* located ~ 9 Å above the 'dimple' in the cluster surface in which it is thought to reside.

The most natural explanation for our experimental results is that excitation onto the upper, $^2\Pi_{3/2}$, surface leads to a rapid formation of the exciplex, while excitation to the lower, $^2\Pi_{1/2}$, surface leads to a slow formation of the exciplex. Due to the low temperature of the He cluster (0.37K), a simple Boltzmann calculation would predict that a 0.7 cm^{-1} barrier could reduce the exciplex formation rate by a factor of 16 and thus account for the experimental findings noted above. Accounting for tunneling effects in a semiclassical calculation, we have found that the height and width of the spin-orbit generated barrier are insufficient in explaining the formation delay we find along the $^2\Pi_{1/2}$ potential curve. It is likely that an accurate modeling of the exciplex formation on the cluster surface will require treatment of the simultaneous interaction of the He atom with both the Na* and the rest of the He atoms that make up the cluster. The energy for evaporation of a He atom from a cluster surface is taken to be 5 cm^{-1}. Thus the barrier through which the He must tunnel may be thought of as a superposition of the He atom-He cluster potential with the NaHe molecular $^2\Pi_{1/2}$ potential. This more complex potential scheme can be seen to increase the height and width of the barrier substantially from that of the simple $^2\Pi_{1/2}$ spin-orbit interaction of Na*He. The model described above will also lead to a barrier, albeit smaller, for the formation of the exciplex on the $^2\Pi_{3/2}$ surface. This is consistent with experimental findings, in which a smaller but finite delay is found for the excimer fluorescence along this surface as well.

2.9 Dynamics of the quartet sodium trimer in the electronic $2^4E'$ state

Time-resolved experiments have been undertaken in order to further our understanding of the energetics and timescales of the relationship between the $2^4E'$ quartet state of Na_3 and the predissociative doublet state into which it can cross. Selective excitation of the various v,j bands of the $2^4E'$ state of Na_3, allow us to study rise and fall times of fluorescence generated by each product channel as a function of excitation energy. In labeling the vibronic bands of the $2^4E'$ state, v is the vibrational quantum number while j is a Jahn-Teller pseudo-rotational quantum number. Introducing band-pass filters which are selective for Na atomic fluorescence (16980 $\pm$ 145 cm^{-1}), singlet Na_2 B $\rightarrow$ X fluorescence (20,000 $\pm$ 198 cm^{-1}), and "resonant" quartet fluorescence (15800 $\pm$ 125 cm^{-1}) allow for selective collection of each reaction product. The resultant rise and fall times for Na atomic and singlet Na_2 B $\rightarrow$ X fluorescence as a function of excitation are presented in Table III. The fall times for the atomic and B $\rightarrow$ X dimer fluorescence are in excellent agreement with the gas phase values for both of these transitions, (16.27 and 6.65 ns, respectively). This good fit eliminates the possibility of the reaction products remaining on the cluster surface at the time of emission. The fall times of the resonant fluorescence are biexponential and are still under analysis. We report preliminarily that the longer of the two fall times (~1.3 ns) seems independent of which vibronic band is excited, while the second, faster, fall time decreases from roughly 1.2 ns for excitation of v,j = 0,0 to about 500 ps for v,j = 4,5/2.

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It can be seen that for a given v, j excitation of the quartet Na_3 the _rise_ times of the atomic and dimeric fluorescence exhibit similar behavior, including the biexponential rise evidenced upon excitation of the two lowest bands of the $2^4E'$ state. This then assures us that the nonadiabatic processes leading to atomic emission and to dimeric emission are one and the same as has been postulated. That is, the channel through which excess energy will be released by photon emission has no bearing on the intersystem crossing into the doublet state. We also note from Table I that the rise times of atomic and dimeric fluorescence become faster and faster as we excite higher bands of the $2^4E'$ state. This signifies that the trimer is more quickly crossing into the doublet manifold with increased excitation energy as the intersystem crossing must occur before any product fluorescence can occur. Further studies monitoring product rise times in the higher v, j bands of the $2^4E'$ state of Na_3 are planned in order to ascertain the vibrational level which most easily allows coupling into the doublet manifold. This information will then serve as a necessary tool in the attempt to map out both the excited quartet and doublet states of Na_3 in a precise manner.

2.10_ Discussion and conclusions

One of the main conclusions derived from the work described above is that in species with a P-type electronic structure, spin orbit coupling plays a role in the formation of dimers and, therefore, also higher clusters. The methods developed in our laboratory to study the formation and low T reactivity of metastable alkali complexes and excimers can be now applied to other species.

We note that the introduction of rare gas matrix isolation spectroscopy was an important step forward in the development of chemistry. For the first time, a large number of "reaction intermediates" that had been previously proposed by chemists could be isolated and studied. More importantly, a great many new, and previously unexpected, chemical species were detected and characterized [22]. Chemists felt the necessity to re-evaluate their definitions of what constituted a chemical species, since many molecules far too fragile to be isolated at room temperature could now be formed and stabilized, and held often for very long periods. The reason for this dramatic change was largely the change in temperature scale which from the values valid for solution chemistry, that previously extended from room temperature down to 200 K, moved down to the 40-80 K domain. Because of the typical exponential dependence of reaction rates on temperature, this modest change in absolute temperature scale led to dramatic changes in the chemistry that became thermally accessible.

The development of spectroscopy of species attached to, and dissolved in highly quantum clusters made of molecular hydrogen ($\approx$ 5 K) and atomic helium (0.37 K) promises another dramatic expansion in our understanding of chemical stability. The fractional change in temperature is even higher than in the case of the development of traditional cryogenic matrix spectroscopy. The size of a chemically significant energy drops from $\approx$ 1 Kcal/mole at room temperature to $\approx$ 1 cal/mole. This implies that a wide range of subtle and delicate chemical effects will dramatically alter the chemical reactivity in these media. As a result, it is expected that many atomic and molecular species that are viewed as unstable even by the standards of traditional matrix spectroscopy, could well be metastable under such conditions. This observation can have profound implications for a range of chemical phenomena, but perhaps none greater than for the HEDM field.

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1) **Spectroscopy of alkali atoms and molecules attached to highly quantum clusters.**
F. Stienkemeier, W. Ernst, J. Higgins and G. Scoles. Proceedings of the HEDM
conference held in Crystal Bay, NV, in June 1994.

2) **Noble gas clusters as matrices for IR spectroscopy,** S. Goyal, D. L. Schutt, and G.
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3) **Laser spectroscopy of alkali-doped He clusters.** F. Stienkemeier, J. Higgins, W.E.
Ernst and G. Scoles. *Phys. Rev. Lett.* **74**, 3592-95 (1995).

4) **On the use of liquid He cluster beams for the preparation and spectroscopy of
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5) **Spectroscopy of alkali atoms and molecules attached to liquid helium clusters.**
F. Stienkemeier, J. Higgins, W.E. Ernst, and G. Scoles. *Z. Physik B.* **98** 413 (1995).

6) **Spectroscopy of alkali atoms and molecules attached to highly quantum clusters.**
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7) **Spectroscopic investigation of alkali-atom doped H_2 and He clusters.** G. Scoles.
Proceedings of the *HEDM Conference* held in Woods Hole (MA.) June 4-7, 1995,
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8) **The interaction of Li atoms with large clusters of n-H_2, p-H_2, and o-D_2, probed
by laser spectroscopy.** G. Scoles. Proceedings of the *HEDM Conference* held in
Boulder (CO). June 5-7, 1996.

9) **Photoinduced chemical dynamics of high-spin alkali trimers.** J. Higgins, C.
Callegari, J. Reho, F. Stienkemeier, W.E. Ernst, K. K. Lehmann, M. Gutowski, and
G. Scoles. *Science***273** 629 (1996).

10) **Spin Polarized Alkali clusters: observation of Quartet States of the Sodium
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11) **Spectroscopy of Alkali Atoms (Li, Na, K) Attached to large Helium Clusters.** F.
Stienkemeier, J. Higgins, C. Callegari, S.I. Kanorsky, W.E. Ernst, and G. Scoles. *Z.
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12) **Beam Depletion Spectroscopy of Alkali Atoms (Li, Na, K) Attached to Highly Quantum Clusters**. C. Callegari, J. Higgins, F. Stienkemeier, and G. Scoles. *J. Phys. Chem.* **A102,** k95 (1998)

13) **Helium Cluster Isolation Spectroscopy – Alkali Dimers in the Triplet Manifold**. J. Higgins, C. Callegari, J. Reho, F. Stienkemeier, W.E. Ernst, M. Gutowski, and G. Scoles. *J. Phys. Chem.* **A102**, 4952 (1998).

14) **Spin-Orbit Effects in the Dynamics of NaHe Exciplex Formation on Helium Clusters**. J. Reho, C. Callegari, J. Higgins, K. K. Lehmann, and G. Scoles. *Faraday Discussions* **108** 161 (1997).

15) **Non-adiabatic effects in the interaction of light metal atoms with hydrogen and helium clusters.** C. Callegari, W.E. Ernst, J. Higgins, K.K. Lehmann, J. Reho and G. Scoles. *HEDM Conference;* held at Chantilly (VA), June 1997, Proceedings.

5_ Interactions

a) Collaborations

1) M. Gutowski (PNL, Richland, WA.). On the calculation of potential energy surfaces involving alkali atoms.

2) H. Rabitz and T.S. Ho (Princeton, Chemistry). On the analytical interpolation of potential energy functions involving alkali atoms.

b) Invited papers presented by the P.I. at national and international meetings.

1) "Laser spectroscopy of high spin alkali metal clusters".
European Physical Society Condensed Matter Division Meeting in Stresa (Italy). April 22-25, 1996.
2) "The Three spin game".
Gordon Conference on Molecular and Ionic Clusters in Barga (Italy).
May 6-10, 1996.
3) "Spectroscopy and dynamics of high spin alkali metal clusters".
Plenary speaker at the Columbus Molecular Spectroscopy Symposium, Columbus (OH). June 10-14, 1996.
4) Conference on Electronic Structure and Reaction Dynamics Okazaki, Japan, March 17-21, 1997.
5) 1997 NAIR Workshop on Cluster Science, Tsukuba, Japan, March 9-15, 1997.
6) Workshop on Quantum Fluid Clusters, Ringberg Schloss Germany, June 15-18, 1997.
7) XVIII International Symposium on Molecular Beams, Paris, France, June 2-6, 1997.
8) Conference on the Dynamics of Molecular Collisions, Gull Lake, Minnesota, July 20-25, 1997.
9) Symposium in the interactions of oriented molecules. Bielefeld, Germany, June 30-July 3, 1997.

In addition, K. K. Lehmann has presented an invited talk at the Gordon Conference on electronic Spectroscopy held in Oxford (U.K.) in August 1997 and W.E. Ernst presented invited talks at the Spring Meeting of the German Phys. Society (Mainz, March 1997), at the March Meeting of the APS (Kansas City, March 1997), and at the EGAS Conference in Berlin (Germany) in July 1997.

c) Invited seminars given by the P.I. on subjects concerning this grant: 20

1) U.C. Berkeley, Chemistry Department, Jan. 23, 1996.
2) K. U. of Nijmegen (The Netherlands) April 15, 1996.
3) Physics Department, University of Padova (Italy) April 29, 1996.
4) European Laboratory for Non Linear Spectroscopy (LENS), Firenze (Italy), April 30, 1996.
5) Physics Department, University of Genova (Italy) May 2, 1996.
6) Physics Department, University of Kaiserslautern (Germany) May 17, 1996.

(7-9)   Three lectures given at the Applied Physics Department of the University of Bonn
        (Germany) July 24, 25 and 31, 1996.
(10)   Max-Planck Institut für Festkörperphysik, Stuttgart (Germany), July 29, 1996.
(11)   University of Tokyo, Chemistry Department, March 21, 1997.
(12)   University of Kyoto, Physics Department, March 21, 1997.
(13)   RIKEN, Wako, Japan, March 24, 1997.
(14)   University of Helsinki (Finland), Phys.Chem.Dept., May 27, 1997.
(15)   University of Leiden (The Netherlands) Physics Dept., May 28, 1997.
(16)   University of Nijmegen (The Netherlands) Physics Dept., May 29, 1997.
(17)   University of Dusseldorf (Germany) Chem. Dept., June 23, 1997.
(18)   Ecole Polytech of Lausanne (Switzerland) Chem Dept., May 23, 1997.
(19)   University of Bonn (Germany) Phys. Dept., June 27, 1997.
(20)   University of Morelos (Cuernevaca, Mexico) Phys. Dept. Sept. 30, 1997.

In addition, K. K. Lehmann has given a talk on the same subject at the Chemistry
Department of Stanford University and W. E. Ernst spoke at the University of Tuebingen
(Germany) on January 8, 1997, in; Darnstadt (Germany) on March 6, 1997,
at Penn State on May 8, 1997, and at the Max-Planck Institute in Göttingen on May 29,
1997.

1) "Laser induced fluorescence and beam depletion spectra of alkali atoms attached to large H_2 and D_2 clusters".
   C. Callegari, F. Stienkemeier, J. Higgins, and G. Scoles.
   Gordon Conference on Molecular and Ionic Clusters in Barga (Italy).
   May 6-10, 1996.
2) "Optical singlet and triplet bands of homonuclear alkali diatomics attached to cold helium clusters"
   J. Higgins, C. Callegari, J. Reho, W. E. Ernst, and G. Scoles
   51st Ohio State University Symposium on Molecular Spectroscopy.
   Columbus (OH), June 10-14, 1996.
3) "Observation of the $2^3\Sigma_g^+ \leftarrow 1^3\Sigma_u^+$ and $1^3\Pi_g \leftarrow 1^3\Sigma_u^+$ transitions of the triplet NaK molecule on the surface of helium clusters"
   J. Higgins, C. Callegari, J. Reho, W. E. Ernst, K. K. Lehmann, and G. Scoles
   51st Ohio State University Symposium on Molecular Spectroscopy.
   Columbus (OH), June 10-14, 1996.

4) "Dispersed fluorescence studies of quartet state alkali trimers"
   J. Higgins, C. Callegari, J. Reho, W. E. Ernst, K. K. Lehmann, and G. Scoles
   51st Ohio State University Symposium on Molecular Spectroscopy.
   Columbus (OH), June 10-14, 1996.
5) "Laser induced fluorescence of K atoms attached to large hydrogen clusters".
   C. Callegari, F. Stienkemeier, J. Higgins, and G. Scoles
   51st Ohio State University Symposium on Molecular Spectroscopy.
   Columbus (OH), June 10-14, 1996.
6) "Large helium clusters as an environment for spectroscopy of high spin alkali dimers and trimers".
   F. Stienkemeier, J. Higgins, C. Callegari, J. Reho, W. E. Ernst, and G. Scoles.
   8th International Symposium on Small Particles and Inorganic Clusters (ISSPIC),
   July 1-6 1996, Copenhagen, Denmark.
7) "Preparation and Spectroscopy of Alkali Aggregates on Cold Helium Clusters".
   J. Higgins, C. Callegari, J. Reho, F. Stienkemeier, W.E. Ernst, and G. Scoles
   14th International Conference on High Resolution Molecular Spectroscopy.
   Prague, Czech Republic, September 9-13, 1996.

8) J. Higgins: "Three-Body Van der Waals Forces in Quartet State Alkali Trimers." J. Higgins, C. Callegari, J. Reho, W. E. Ernst, M. Gutowski, K. K. Lehmann, and G. Scoles. 1997 March Meeting of the American Physical Society. Kansas City, MO. March 17-21, 1997.

9) J. Higgins: "The Effects of a Helium Nano-Droplet Matrix on the Electronic Spectroscopy of Sodium Dimers." J. Higgins, C. Callegari, J. Reho, W. E. Ernst, and G. Scoles. 52nd Ohio State University International Symposium on Molecular Spectroscopy. Columbus, OH. June 16-20, 1997.

10) J. Higgins: "The Spectroscopy of Alkali Dimers and Trimers on the Surface of Helium Clusters at 0.4 Kelvin." J. Higgins, C. Callegari, J. Reho, W. E. Ernst, K. K. Lehmann, and G. Scoles. Workshop on High Resolution Multiple Resonance Spectroscopy. Storrs, CT. June 25-26, 1997.

11) J. Reho: "Time Resolved Laser Induced Dynamics of Excited Alkalis on Helium Clusters." J. Reho, J. Higgins, C. Callegari, K.K. Lehmann, and G. Scoles. 52nd Ohio State University International Symposium on Molecular Spectroscopy. Columbus, OH. June 16-20, 1997.

12) J. Reho: "Time Resolved Spectroscopy of Na Atoms and Oligomers on the Surface of He Clusters." J. Reho, C. Callegari, J. Higgins, K.K. Lehmann, and G. Scoles. The 13th Annual University of Waterloo Symposium on Chemical Physics, Waterloo, Ontario, Canada, October 24-26, 1997.

13) M. Radcliff: "Non-adiabatic Processes in the Photodissociation of Quartet State Na Trimer." J. Reho, J. Higgins, M. Radcliff, K.K. Lehmann, and G. Scoles. The 13th Annual University of Waterloo Symposium on Chemical Physics, Waterloo, Ontario, Canada, October 24-26, 1997.

14) C. Callegari: "He Clusters as a Matrix for Preparation of Na-$(H_2)_n$ Complexes." C. Callegari, J. Higgins, J. Reho, G. Scoles. 52nd Ohio State University International Symposium on Molecular Spectroscopy. Columbus, OH. June 16-20, 1997.

15) C. Callegari: "Singlet Na_2 Molecule as a Probe of the Excitations in Liquid Helium Clusters." C. Callegari, J. Higgins, J. Reho, G. Scoles. 1997 March Meeting of the American Physical Society. Kansas City, MO. March 17-21, 1997.

16) G. Scoles: "Helium Cluster Isolation Spectroscopy of Alkali Atoms in the Triplet Manifold." J. Higgins, C. Callegari, J. Rego, F. Stienkemeier, W.E. Ernst, and G. Scoles. The 13th Annual University of Waterloo Symposium on Chemical Physics, Waterloo, Ontario, Canada, October 24-26, 1997.

6_ PI Honors and Awards

The PI was a plenary speaker at the Columbus Meeting where he was presented with the 1995 Lippincott Award of the Coblentz Society, the OSA and the SAS for his contributions to Molecular Spectroscopy.
In May 1996 the PI was awarded an honorary doctorate in Physics by the University of Genova, Italy.
During 1996 the PI was an A. von Humboldt Foundation Awardee and visited numerous research laboratories in Germany over a period of four months.
The PI is a fellow of the American Physical Society and of the Canadian Society for Chemistry, and received in 1987 a Senior Killam Fellowship from the Killam Foundation of Canada.
On May 15, 1997 the P.I. was elected Fellow of the Royal Society (the National Academy of the Sciences of the U.K.).
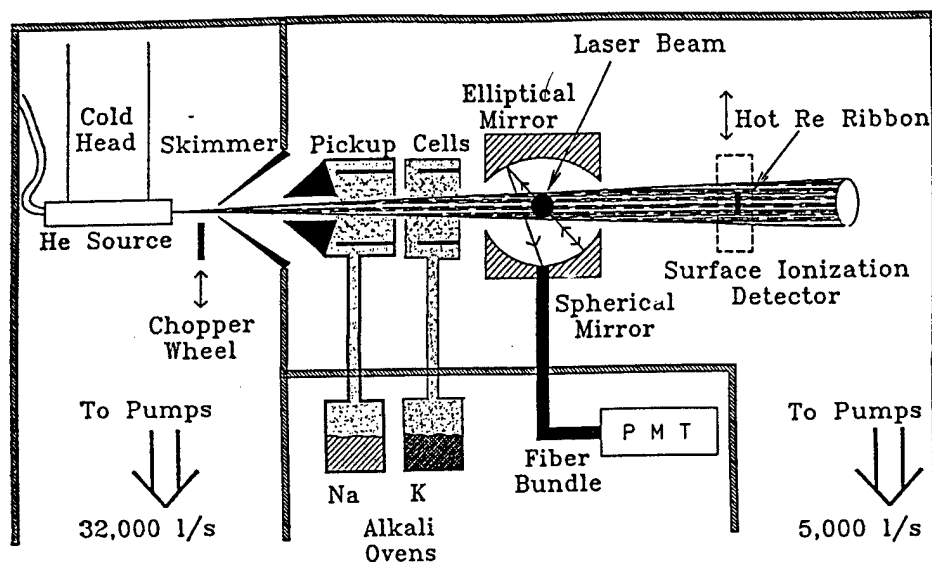
Fig. 1 Experimental apparatus for laser induced fluorescence and surface ionization spectroscopy of alkali-doped condensed gas clusters.
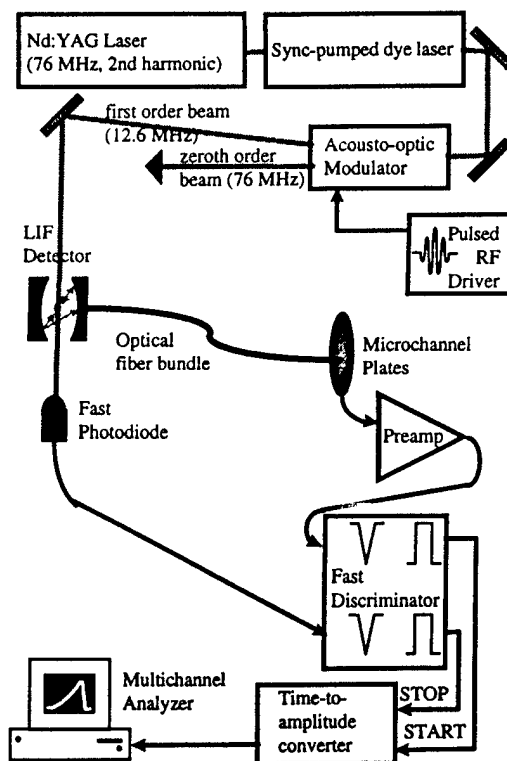

Figure 2. Schematic of the Time-correlated single photon counting apparatus
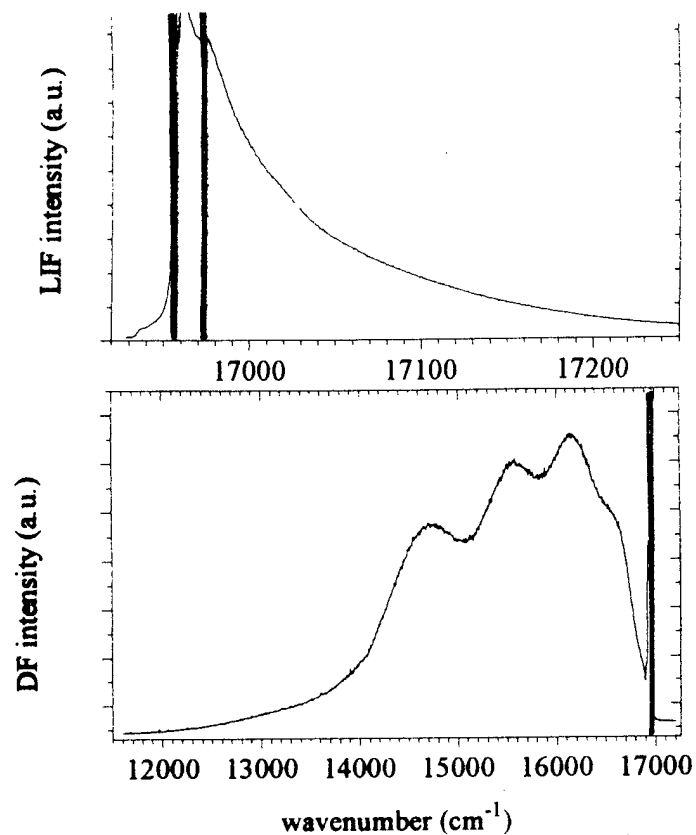
Figure 3. Laser Induced Fluorescence (top, continuous line), Beam Depletion (top, dashed line) and Dispersed Fluorescence (bottom) Spectra of Na on the surface of He clusters. The position of the gas phase D lines is marked by the grey bars.
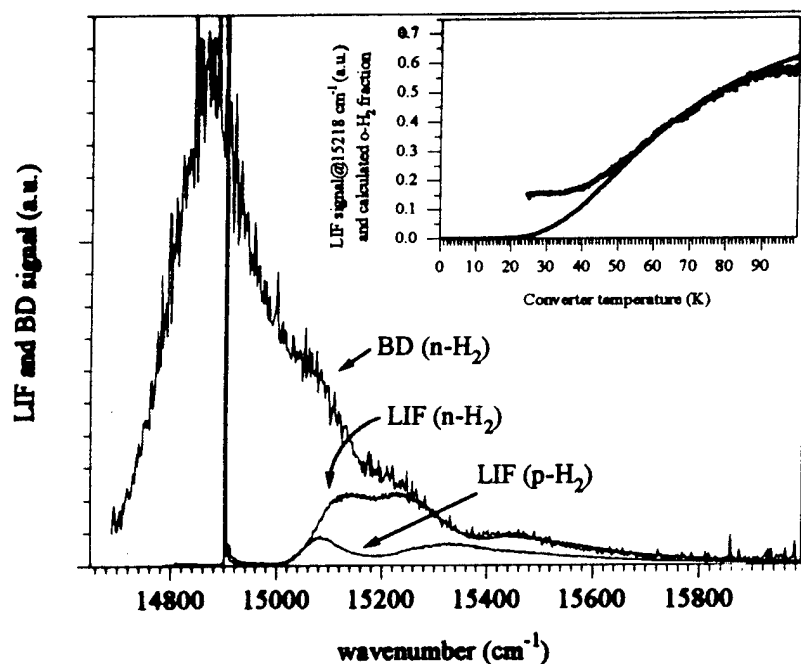

Figure 4. LIF and BD spectra of LI atoms on *normal-* and *para-*H_2 clusters. The inset shows the calculated *ortho-*H_2 fraction (gray line) and LIF intensity of Li atoms on H_2 clusters at 15218 cm^{-1} excitatation frequency (dots) as a function of the *ortho-para* converter temperature.
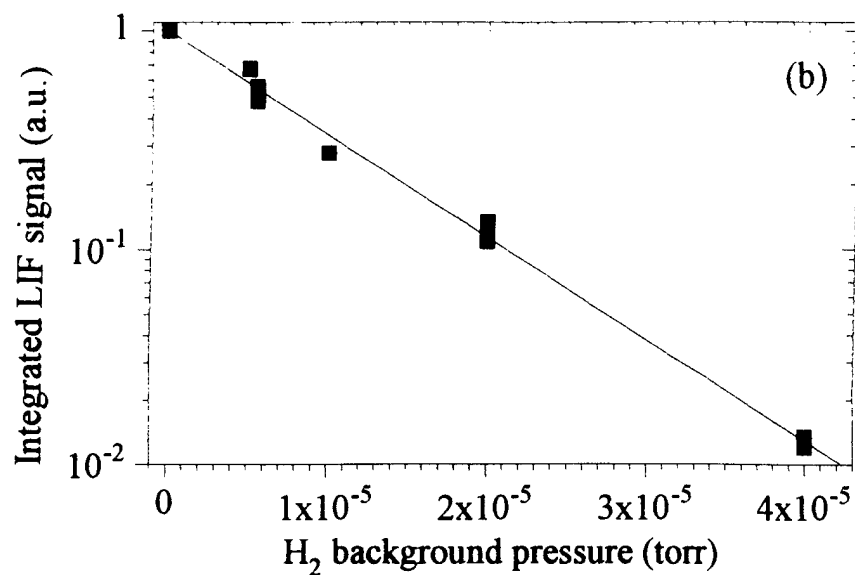
Figure 5. Integrated LIF signal of Na-$(H_2)_n$ complexes on the surface of He clusters as a function of background H_2 pressure. The straight line is a fit to an exponential decay.

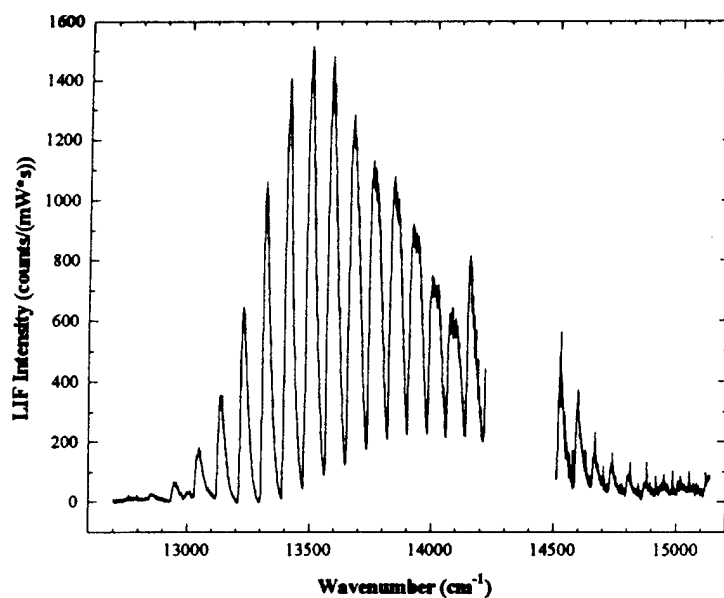Figure 6. Excitation spectrum of the $1^3\Sigma^+_g \leftarrow 1^3\Sigma^+_u$ transition of Na_2 on the surface of helium clusters. The v'=6-29 bands are displayed in the figure.

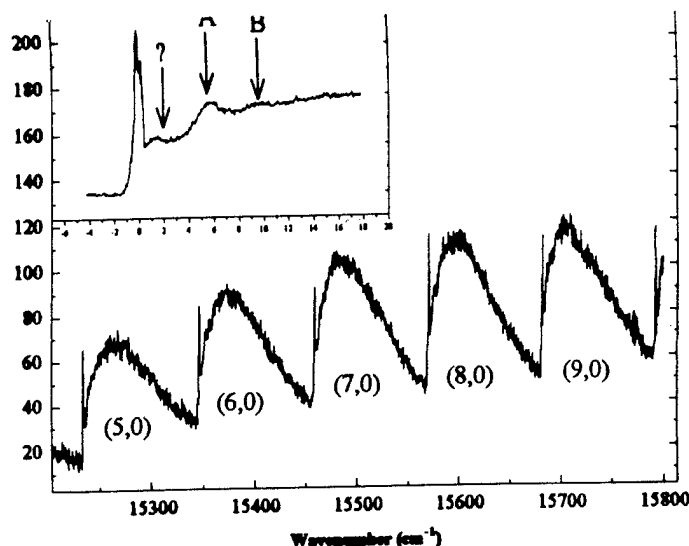Figure 7. Excitation spectrum of the $1^1\Sigma^+_u \leftarrow 1^1\Sigma^+_g$ transition of Na_2. Inset reveals the high resolution structure associated with the zero-phonon line region for the (9,0) band. A and B arrows denote the predicted position of roton and maxon excitations in bulk liquid helium. The feature indicated by the arrow with a question mark is presently unassigned.
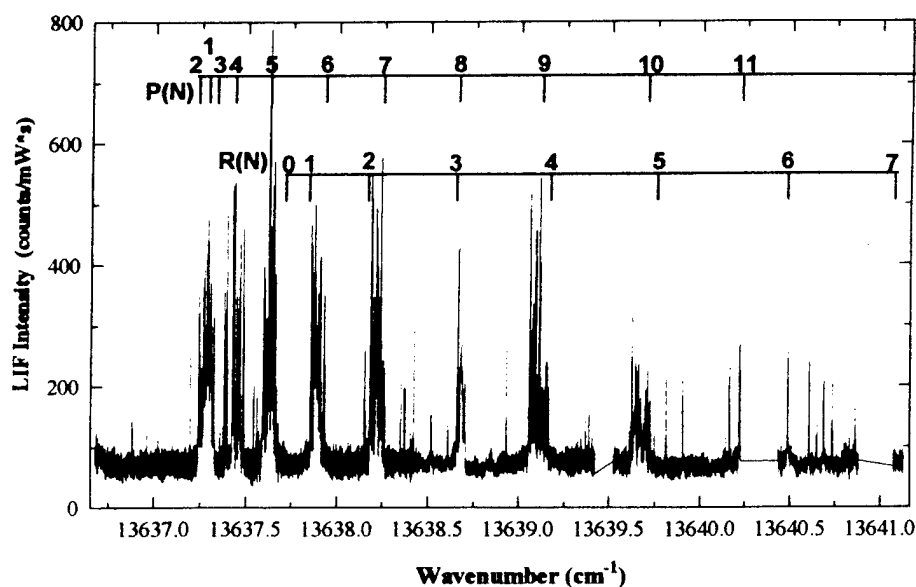

Figure 8. Excitation spectrum of the $1^3\Sigma^+_g \leftarrow 1^3\Sigma^+_u$ transition of Na_2 desorbed from the surface of helium clusters. The dimers are formed on helium clusters and subsequently enter the gas phase as revealed by the narrow linewidth (~80 MHz) the rotational lines. The rotational assignments are based on the work of Farbert et al. (FAR 95) where the dimers were formed in a conventional molecular beam expansion of sodium gas.
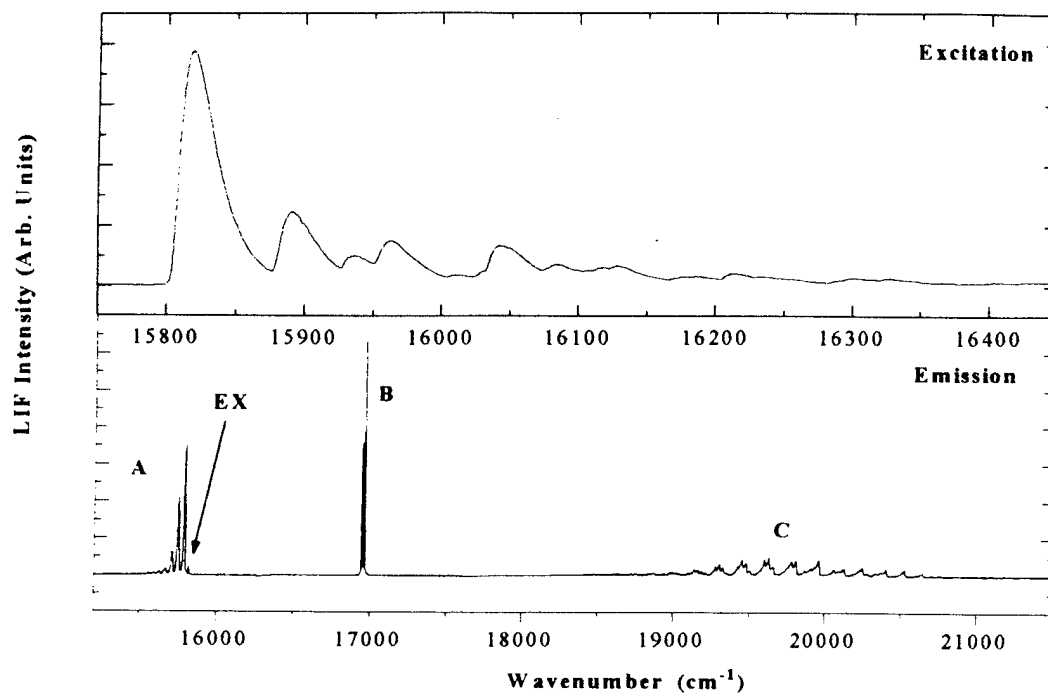
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Figure 9. Excitation and emission spectra of the $2^4E' \leftarrow 1^4A_2'$ transition of Na_3. Excitation frequency is marked by EX.
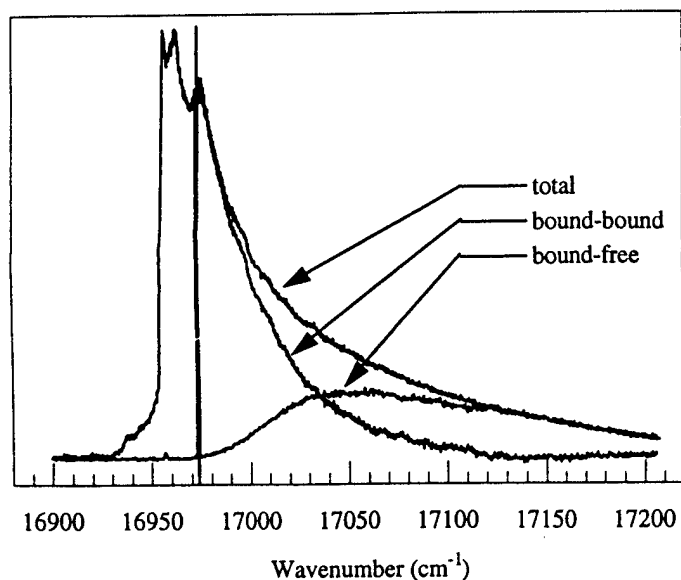
Figure 10. Excitation spectrum of Na atoms on He clusters illustrating that the total spectrum is composed of bound-free and bound-bound contributions. The bound-free contribution is measured by monitoring fluorescent emission at the gas phase lines. The bound-bound contribution is determined by collecting red-shifted fluorescent emission.

Fluorescence at 16980 ± 145 cm^{-1} (free atoms)

Excitation energy (cm^{-1})	Rise Time (ps)	Fall Time (ns)
17041	50 ± 20	16.3 ± 0.1
17084	50 ± 20	16.3 ± 0.1
17127	70 ± 20	16.2 ± 0.1
17385	70 ± 20	16.2 ± 0.1

Fluorescence at 15800 ± 125 cm^{-1} (excimers)

Excitation energy (cm^{-1})	Rise Time (ps)	Fall Time (ns)
16945	700 ± 20	18.2 ± 0.1
16956	700 ± 20	18.2 ± 0.1
16973	80 ± 20	20.1 ± 0.1
16994	70 ± 20	20.7 ± 0.1
17041	80 ± 20	21.2 ± 0.1

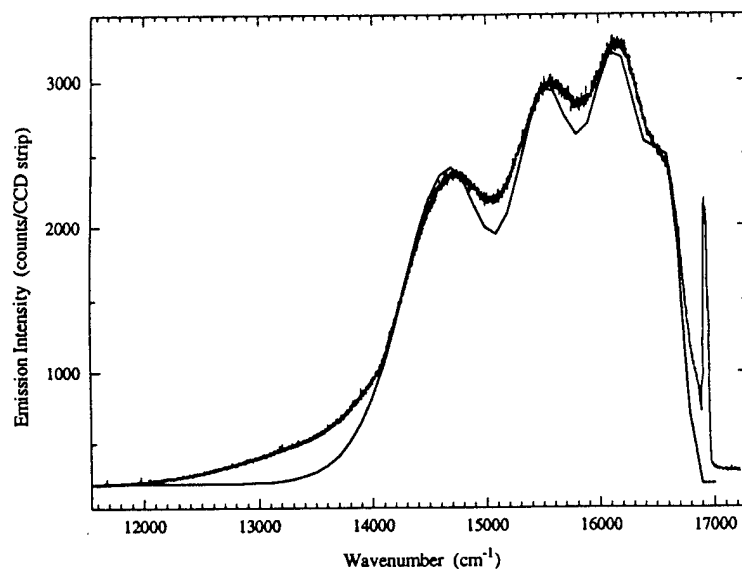Table I. Time-resolved fluorescence rise and fall times for Na atoms on He clusters.

Figure 11. Dispersed fluorescence spectrum of Na*-He excimers desorbed from He clusters after excitation of Na atoms on the surface of the cluster. The excitation energy is 16975 cm^{-1}.

Excitation Energies

	16954.6	16960.7	16975.2	17046.7	17150.7
v = 0	0.35	0.33	0.30	0.24	0.10
v = 1	0.34	0.34	0.32	0.25	0.22
v = 2	0.24	0.25	0.26	0.26	0.27
v = 3	0.07	0.08	0.12	0.25	0.41

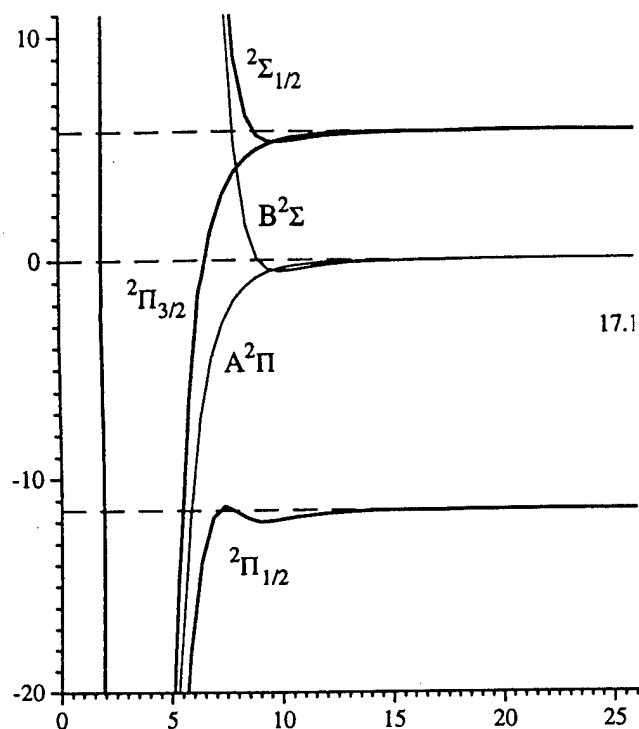Table II. Na*-He vibrational levels populations after excitation of Na atoms on He clusters at different energies.

Figure 12. Long-range view of Na*-He potentials, neglecting (thin lines) and including (thick lines) the spin-orbit perturbation. Energies are relative to the unperturbed asymptotic value (16975.8 cm^{-1})

Excitation Energy (cm^{-1})	Quantum Numbers (v,j)	Na$_2$ B$\rightarrow$X Rise Time ($\pm$20 ps)	Na$_2$ B$\rightarrow$X Fall Time ($\pm$0.01 ns) (Lifetime)	Na P$\rightarrow$S Rise Time ($\pm$20 ps)	Na P$\rightarrow$S Fall Time ($\pm$0.01 ns) (Lifetime)
15818	0,0	1380/1550	6.65	770/2100	16.28
15892	1,1/2	890/990	6.65	770/1100	16.26
15936	2,5/2	427	6.68	445	16.24
15963	2,1/2	385	6.65	434	16.28
16044	3,1/2	370	6.67	417	16.29
16084	3,5/2	385	6.64	434	16.28
16118	4,5/2	222	6.65	345	16.26

Table III. Rise and fall times of Na atomic (P$\rightarrow$S) and Na$_2$ singlet dimer (B$\rightarrow$X) fluorescence generated by excitation of the 2^{4}E$'$ state of Na$_3$.